



Short communication

Copper vanadate as promising high voltage cathodes for Li thermal batteries

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H I G H L I G H T S

- We synthesized series of the $\text{CuO}-\text{V}_2\text{O}_5$ oxides, namely CuV_2O_6 , $\text{Cu}_2\text{V}_2\text{O}_7$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$.
- The structure and morphology have been alloy have been investigated.
- We determined the electrochemical properties at room temperature and elevated temperatures (525 °C) against Li.
- Copper-vanadate materials are found to be high voltage cathodes for thermal Li batteries.

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In this original work, series of the $\text{CuO}-\text{V}_2\text{O}_5$ oxides, such as CuV_2O_6 , $\text{Cu}_2\text{V}_2\text{O}_7$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$ have been synthesized and evaluated as possible candidate cathode materials in high voltage Li thermal batteries. The structure and morphology have been determined and the electrochemical properties at room temperature and elevated temperatures (525 °C) against Li metal alloy have been investigated. At room temperature, an increase in copper content in the vanadate has been found to provoke a gradual negative shift of the operating voltage plateau vs. Li metal. Room temperature discharge capacity in a Li cell is relatively high and can exceed 350 mAh g^{-1} . In a thermal Li cell configuration and at an elevated temperature a voltage plateau of 3.4 V at a current load of 100 mA g^{-1} was achieved and a voltage plateau of 2.5 V was recorded with a current load of as high as 310 mA g^{-1} . Thus, copper-vanadate materials may be regarded as promising short time – high voltage cathodes for thermal Li batteries.

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1. Introduction

Pyrite is regarded as the dominant cathode material being currently used in thermal batteries [1], although its performance is limited due to its low working temperature (525 °C) and the relatively low discharge potential plateau (only 2 V). These two limiting parameters have a tremendous effect on the discharge time (and hence on the associated capacity), as well as on the overall weight and size of the battery.

Discharge time is being measured from the time the battery is being ignited, when temperature rises to approximately 525 °C, which constitutes 150–250 °C above the melting temperature of the electrolyte. Once the electrolyte melts, discharge is being initiated and the reaction ends as the electrolyte solidified (freezes), leading to a halt in ion migration or simply causing depletion in reactants concentrations. In order to extend the operating time of the battery

(and hence the cell capacity), the electrolyte must remain in its liquid state, and therefore, an effective thermal insulation must be designed around battery components, decreasing the overall cooling rate. Temperature rise toward a targeted high temperature values, such as 525 °C is determined by the stability of the battery components. This concerns the stability of the cathode, electrolyte and anode, as well as any interaction between the components, such as cathode/electrolyte and anode/electrolyte.

On the temperature limitation issue, it should be noted that pyrite decomposes at 580 °C, forming a nonstoichiometric monosulfide (pyrrhotite) and sulfur vapor, which react exothermically with the lithium, lithium-alloy anode or dissolved lithium in the molten electrolyte [2]. Increasing the critical temperature may enable extending the operation time of the battery, since higher working temperature will increase discharge time, assuming equal heat insulation. The size of a battery is an important factor in small systems engineering, and thus, decreasing the battery size will enable a design flexibility, which can be achieved with the use of thin films instead of thick discs electrodes [3,4]. In addition, increasing the overall working cell potential will allow a substantial

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decrease in the battery weight and dimensions. Pyrite discharge potential at a current density of 100 mA g^{-1} is about 2 V [5] and thus, a development of cathode materials that can deliver higher working potential will significantly increase the cell energy density and will lead to a decrease in the overall cells volume assembled in the battery.

Copper vanadates have high voltage, high capacity [6–8] and high temperature stability (Fig. 1). Vanadium pentoxide V_2O_5 [3] and copper oxide CuO [10] were previously evaluated as possible cathodes in thermal batteries. $\text{CuO-V}_2\text{O}_5$ phase diagram is presented in Fig. 1, and it can be easily observed that the vanadium richest compound known to exist in this system of oxides is CuV_2O_6 ($n = 1$). The crystal structure of $\alpha\text{-CuV}_2\text{O}_6$ and that of $\text{Cu}_5\text{V}_2\text{O}_{10}$ was already determined and reported elsewhere [11,12]. Electrochemistry (charge and discharge behavior) of $\text{Cu}_5\text{V}_2\text{O}_{10}$ was reported by Sakurai et al. and Eguchi et al. [6,13]. Among the divalent Metal-vanadates that are reported to reversibly intercalate lithium, copper vanadate provides an impressive cell voltage and energy density [8]. Among the mixed oxide materials having multi redox systems, $n \text{ CuO-V}_2\text{O}_5$ have also an appreciable advantage due to the preferential reduction of Cu^{+2} over V^{+5} during the oxidation of the lithium anode in the first stage of discharge, followed by a dual redox of $\text{Cu}^{+2} \rightarrow \text{Cu}^{+1}$ and $\text{V}^{+5} \rightarrow \text{V}^{+4}$ reactions. At the end of the discharge process, the preferential redox is the $\text{V}^{+5} \rightarrow \text{V}^{+4}$. Detailed explanation is provided in [14].

Sakurai et al. [6] found that Li extraction occurs quite easily, leading to a relatively minor expansion in the interlayer spacing while Cu^{+2} in the oxide is reduced to form a metallic copper. The aim of this short report is to present a genuine study on the development of cathode materials for thermal batteries based on copper-vanadates materials that provide both higher working temperature and voltage. As far as the authors are aware of, this is the first time such approach and results are being demonstrated.

2. Experimental

Copper vanadates host materials cathodes such as $\alpha\text{-CuV}_2\text{O}_6$, $\alpha\text{-Cu}_3\text{V}_2\text{O}_8$, $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$, $\text{Cu}_5\text{V}_2\text{O}_{10}$ were synthesized by a solid state reaction from CuO and V_2O_5 powders in three different molar ratio, 1:1, 2:1, 3:1 and 5:1, respectively. The materials were mixed and

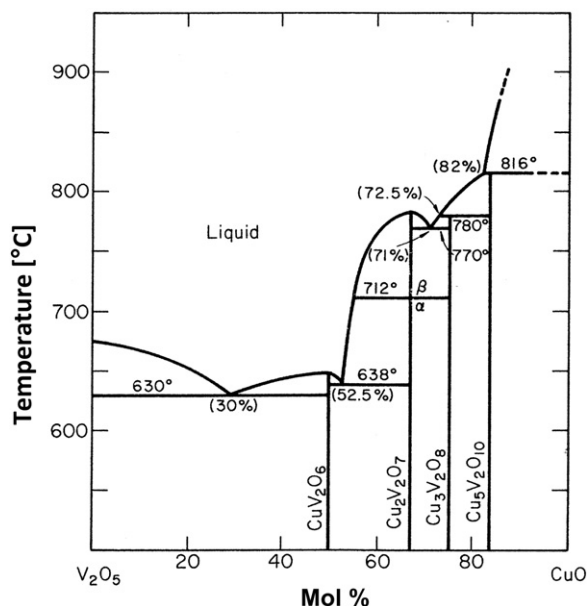


Fig. 1. $\text{CuO-V}_2\text{O}_5$ phase diagram [9].

Table 1
Copper vanadates synthesis procedures.

Cathode material	Molar ratio		Synthesis				
	CuO	V_2O_5	Temperature ^a [°C]	Time [hour]	Heating rate [°C h ⁻¹]	Cooling rate [°C h ⁻¹]	Ref
$\alpha\text{-CuV}_2\text{O}_6$	1	1	620	48	60	60	[14]
$\alpha\text{-Cu}_2\text{V}_2\text{O}_7$	2	1	680	72	60	60	[15]
$\text{Cu}_3\text{V}_2\text{O}_8$	3	1	700	72	60	60	—
$\text{Cu}_5\text{V}_2\text{O}_{10}$	5	1	800	72	60	60	[13]

^a A few temperature steps preceded calcination temperature.

grounded using a planetary ball mill, pressed into pellets and dried at 120°C for 1 h. Synthesis of $\alpha\text{-CuV}_2\text{O}_6$ was conducted in a tube furnace; temperature was increased slowly at a constant rate (1°C h^{-1}) to 620°C and was maintained at this level for 48 h. Afterward, a slow cooling at constant rate (1°C h^{-1}) to room

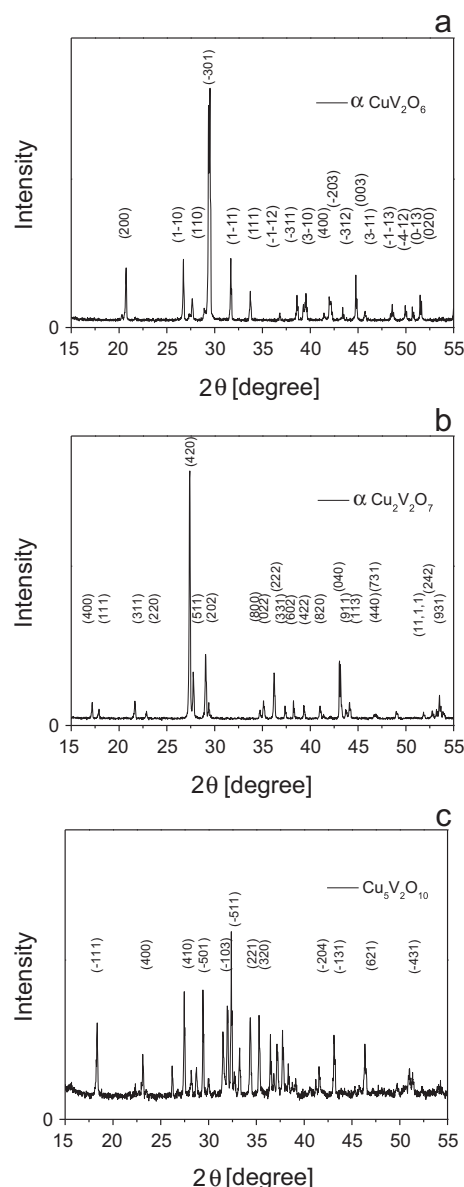


Fig. 2. XRD Pattern of single phases $\alpha\text{-CuV}_2\text{O}_6$ (a); $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$ (b); and $\text{Cu}_5\text{V}_2\text{O}_{10}$ (c).

temperature was processed. Synthesis of α - $\text{Cu}_2\text{V}_2\text{O}_7$, $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$ were performed at temperatures of 680, 700 and 800 °C, respectively. Materials were kept in the furnace for duration of 72 h (the reader is guided to the synthesis conditions description provided in Table 1).

Fabrication of the composite cathode materials for room temperature electrochemical evaluation was made by thoroughly mixing copper vanadates with 10% carbon black (99.9% Alfa Aesar) and 10% poly(vinylidene fluoride) (PVDF, Aldrich). 1-methyl-2-pyrrolidone (NMP, Merck 99.5%) was added to liquefy the powder into slurry. The slurry was casted on a pure aluminum foil using a 15 mils Doctor blade. The Al foil with the cathode material was placed in a vacuum oven at 110 °C for 1 h, then cooled and cut to 1 cm² discs.

X-Ray diffraction analysis was conducted in order to examine the cathode phases using a conventional X-ray powder diffractometer (Philips X'Pert Diffractometer, Eindhoven, The Netherlands) having a $\text{CuK}\alpha$ tube, operated at 40 mA and 40 kV. High resolution scanning electron microscopy (HRSEM, LEO 982 Gemini microscope equipped with a field emission gun (FEG–SEM)) was used to study the morphology of the cathode powder.

The electrochemical cell used for ambient evaluation was a “T cell” type and the electrolyte was composed of ethylene carbonate/dimethyl carbonate (EC/DMC) mixture in a volume ratio of 1:1 containing 1 M LiPF_6 . Galvanostatic (current density of 0.1 mA cm^{−2} (± 0.5 μA)) discharge processes with a cut-off potential of 2 V were conducted using Maccor 2200 series. Elevated temperature discharge measurements were performed at a temperature of 525 °C using a home-built instrument. The cell was assembled from a pelletized cathode material 1–1.5 mm in thickness having a diameter of 30 mm, LiAl (80 weight % Al) anode, KCl and LiCl (weight ratio of 50:50) and MgO separator. To prevent spillage, all 3 components comprising anode, separator and cathode were captured by a ceramic ring and were mechanically isolated (top and bottom) with Mica. The measurements were conducted under a dry air atmosphere (2–3% humidity). The cells were introduced into a preheated oven set to the test temperature. While heating, the electrolyte melts and voltage starts to rise. For stabilization, the cell was maintained at its open circuit potential (OCP) for a short duration of 30 s and only then a current load was applied.

The cathode materials were subjected to Differential Scanning Calorimetry (DSC) and Thermo-Gravimetric Analysis (TGA) (TA Instruments) evaluations. The measurements were conducted from room temperature up to 600 °C in order to confirm the cathode materials thermal stability through heating and above the expected discharge temperature of 525 °C. Measurements were conducted at a thermal ramping rate of 5 °C min^{−1}.

3. Results and discussion

3.1. Cathode material characterization

Synthesized CuV_2O_6 , $\text{Cu}_2\text{V}_2\text{O}_7$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$ materials were studied by a powder x-ray diffraction (presented in Fig. 2) and were identified as single phases of α - CuV_2O_6 , α - $\text{Cu}_2\text{V}_2\text{O}_7$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$ corresponding to JCPDS 30-0513, 26-0566 and 33-0504, respectively. $\text{Cu}_3\text{V}_2\text{O}_8$ was near single phase (JCPDS 00-026-0567), with minor contamination of $\text{Cu}_2\text{V}_2\text{O}_7$ (JCPDS 00-49-0689).

The morphologies of the materials were evaluated by SEM and are presented in Fig. 3. The morphology of the CuV_2O_6 (Fig. 3a) is rounded and with a closer look it is revealed that the structure is a layered one (Fig. 3b), and it is assumed that the layers detected are probably (301) planes. Alpha $\text{Cu}_2\text{V}_2\text{O}_7$ is being characterized by a smaller grain size possessing a different morphology and looks as a “broken one” (Fig. 3c and d). On the other hand, $\text{Cu}_5\text{V}_2\text{O}_{10}$ does not possess broken faced grains and is quite similar to the morphology of the CuV_2O_6 , albeit layered structure is significantly less visible (Fig. 3e and f). It is assumed that the layered CuVO structure, well observed in the SEM, is kinetically supporting a rather fast lithium ion extraction.

3.2. Discharge at room temperature

First galvanostatic discharge curves of α - CuV_2O_6 , α - $\text{Cu}_2\text{V}_2\text{O}_7$, $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$ cathode materials at room temperature are presented in Fig. 4. Discharge were performed at a current density of 0.1 mA cm^{−2}. These curves reveal a well expected behavior for α - CuV_2O_6 [14], α - $\text{Cu}_2\text{V}_2\text{O}_7$ [7] and $\text{Cu}_5\text{V}_2\text{O}_{10}$ [13]. The discharge capacities of the cathode materials are relatively high and approach values of 280–410 mAh g^{−1}. Based on data analysis, shown in Fig. 5,

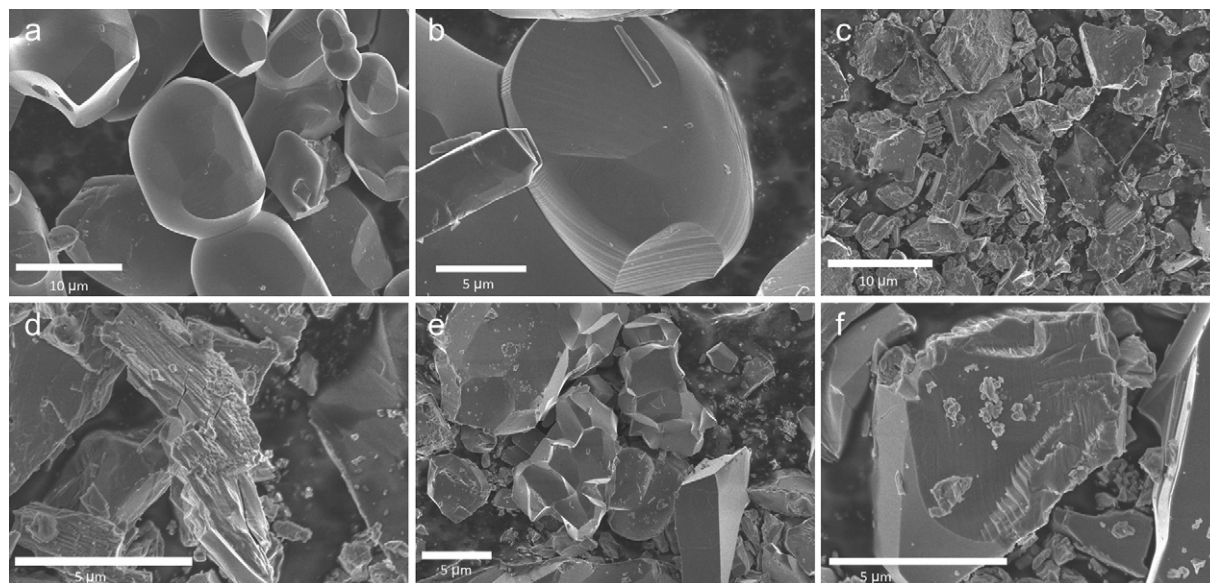


Fig. 3. SEM photographs of α - CuV_2O_6 particles (a, c); a single α - CuV_2O_6 particle representing the layered structure characteristics (b, d); $\text{Cu}_5\text{V}_2\text{O}_{10}$ particles (e); a single α - $\text{Cu}_5\text{V}_2\text{O}_{10}$ particle, representing the layered structure characteristics (f).

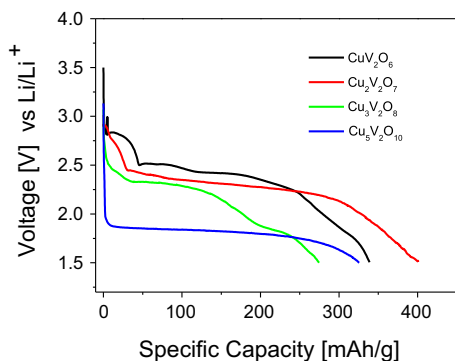


Fig. 4. Room temperature galvanostatic discharge curves of α - CuV_2O_6 , α - $\text{Cu}_2\text{V}_2\text{O}_7$, $\text{Cu}_3\text{V}_2\text{O}_8$ and $\text{Cu}_5\text{V}_2\text{O}_{10}$, at a current density of 0.1 mA cm^{-2} .

and the data accumulated on these materials [7,13,14], it is clear that an increase in copper content in the vanadate provokes a negative shift in the discharge potential plateau. This occurs with a sharp potential reduction for the highest copper content material being evaluated in this study ($\text{Cu}_5\text{V}_2\text{O}_{10}$).

The value of the potential plateau is mainly determined by ion transport rate [14]. Longer diffusion path (or higher concentration polarization) for Li^+ ions and complex 3D structure are expected when larger grains are formed [16]. In this case, diffusion becomes the rate determining step for the electrochemical process. The potential plateau decrease observed by going from α - CuV_2O_6 to α - $\text{Cu}_2\text{V}_2\text{O}_7$, might be explained as well by the stronger V–O–Cu–O bond strength. In fact, Eguchi [14] determined the dependence of the OCP (which is closely related to Nernst potential, E^0) on the extent of lithiation of copper vanadium oxides. It was suggested that Cu^{+2} ions were reduced preferentially over V^{+5} ions and are mainly responsible for electron acceptance, due to the fact that the nobler redox system is $\text{Cu}^{+2}-\text{Cu}^{+1}$, compared with $\text{V}^{+5}-\text{V}^{+4}$ transition. Concerning the copper vanadates $n\text{CuO}-\text{V}_2\text{O}_5$, a drop in OCP and E^0 from 3.3 to 3.1 V vs. Li^+/Li progressing from $n = 1$ (for CuV_2O_6) to $n = 5$ (for $\text{Cu}_5\text{V}_2\text{O}_{10}$) is directly related to the increase in the relative proportion of copper in the vanadates [14].

3.3. Cell discharge at elevated temperature

Data on the high stability of the Galvanostatic discharge profiles for only the CuV_2O_6 and α - $\text{Cu}_2\text{V}_2\text{O}_7$ vanadates obtained from cell operation at elevated temperature of 525°C are presented in Fig. 6. Data extraction and analysis of Fig. 6 discharge curves is shown in Table 2. CuV_2O_6 and α - $\text{Cu}_2\text{V}_2\text{O}_7$ vanadates were further analyzed at elevated temperature since both materials possess the best performance at room temperature among the 4 tested copper

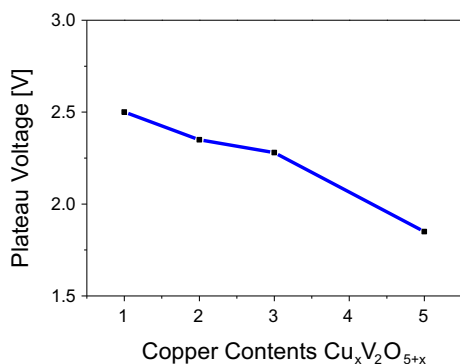


Fig. 5. Plateau potential vs. number of copper atoms content in the various copper vanadates.

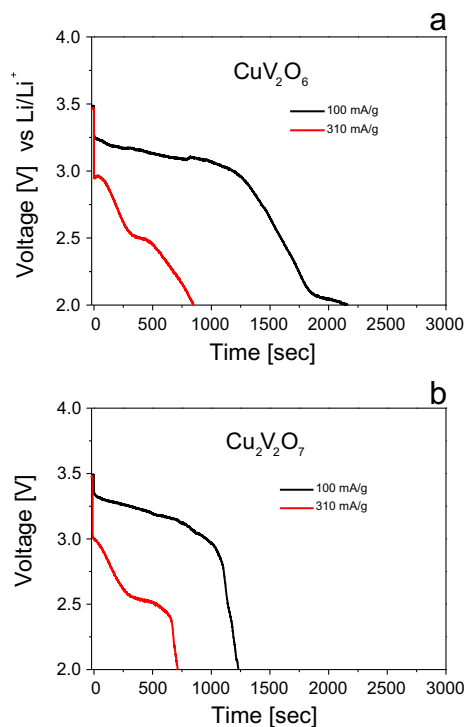


Fig. 6. High temperature galvanostatic discharge curves of α - CuV_2O_6 (a) and α - $\text{Cu}_2\text{V}_2\text{O}_7$ (b) performed at current densities of 100 and 310 mA g^{-1} .

Table 2

Data analysis of high temperature discharge of α - CuV_2O_6 and α - $\text{Cu}_2\text{V}_2\text{O}_7$.

Cathode material	Discharge current [mA g^{-1}]	Time to 3 V cut-off [sec]	Time to 2.4 V cut-off [sec]	Time at 2.4 V plateau [sec]
α - CuV_2O_6	100	1200	—	—
	310	—	550	105
α - $\text{Cu}_2\text{V}_2\text{O}_7$	100	950	—	—
	310	—	660	350

vanadates, as was illustrated in Fig. 3. Prior to the electrochemical evaluations at elevated temperature of 525°C , we have analyzed the materials thermal stability up to a temperature of 600°C . Further data on the thermal stability may found is Figs. 1S and 2S (Supplementary materials).

The behavior of the two cathodes seems at first glance quite similar, as the OCP is the same (3.51 V). The higher copper content electrode (α - $\text{Cu}_2\text{V}_2\text{O}_7$), has a slight disadvantage over the lower copper content electrode material, α - CuV_2O_6 . This is being expressed in the potential plateau values recorded at a current density of 100 mA g^{-1} , as well as its discharge duration. The capacity recorded for the low copper content vanadate (α - CuV_2O_6) is smaller by 25%. Discharging the Li thermal cell at a current density of 310 mA g^{-1} leads to a drastic drop in the potential to a value of 2.4 V. Differences in plateau capacity can be also observed, and the cell utilizing α - $\text{Cu}_2\text{V}_2\text{O}_7$ electrode extends its capacity over a longer period (350 s), while the cell utilizing the α - CuV_2O_6 cathode material was operating for only 105 s, before reaching its cut-off potential.

4. Conclusions

Room and high temperature discharge behavior of selected synthesized copper vanadates were presented in this novel work.

At room temperature, an increase in copper content in the vanadate matrix has been resulted in a gradual negative shift in the potential plateau during discharge, leading to a major reduction in the operational voltage of the cell. In general, room temperature discharge capacity is relatively high and can exceed a capacity of 400 mAh g⁻¹.

At a temperature of 525 °C, the value of the working potential plateau recorded for the electrode having a higher content of copper is above 3 V. Potential values of 3.4 V plateau at a current density of 100 mA g⁻¹ for α CuV₂O₆ and 2.5 V plateau at 310 mA g⁻¹ for α Cu₂V₂O₇ can define copper vanadates [α CuV₂O₆, α Cu₂V₂O₇] as promising candidates for both long time [high voltage (3.4 V) and relatively low currents] and short time [medium-high voltage (2.5 V) and high currents] in thermal batteries applications.

Thermal analysis of both α CuV₂O₆ and α Cu₂V₂O₇ reveal high thermal stability up to a temperature of 600 °C. Based on the phase diagram and thermal analysis results presented here (Supplementary materials section), no phase transformation is being anticipated even up to the melting point of these materials. Thus, the initial ignition temperature can be further increased with the introduction of these promising cathode materials, in order to improve migration rate and operation time.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2012.11.128>.

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